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Spectroscopic evidence for an intramolecular C–H···N hydrogen bond: infrared and Raman spectroscopy and ab initio molecular orbital calculations of *N*,*N*-dimethylpropylamine and propyltrimethylammonium bromide

Keiichi Ohno*, Akimitsu Tonegawa, Hiroshi Yoshida, Hiroatsu Matsuura

Department of Chemistry, Faculty of Science, Hiroshima University, Kagamiyama, Higashi-Hiroshima 739, Japan

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Abstract

The infrared and Raman spectra were measured for *N*,*N*-dimethylpropylamine (DPA) in an argon matrix, the liquid and glassy states and aqueous solution, and for propyltrimethylammonium bromide (PTAB) in the solid state and aqueous solution. The ab initio molecular orbital calculations were performed on possible conformers of DPA and propyltrimethylammonium ion. In an argon matrix, the conformational stability of DPA is in the order G′G > GT > TT, which agrees with the prediction by ab initio calculations. The experimentally confirmed high stability of the G′G conformer indicates that an appreciably strong attractive interaction occurs between the methyl hydrogen atom and the nitrogen atom. This interaction may be called the intramolecular 1,4-C–H···N hydrogen bonding. In the liquid and glassy states, the GT conformer is the most stable. In aqueous solution of DPA, the GT and TT conformers are more stabilized than in the neat liquid, possibly because of the formation of more significant intermolecular hydrogen bonds between the nitrogen atom of DPA and water molecules. For PTAB, only the T conformer exists in the solid state, and this conformer is more stable than the G conformer in aqueous solution. The GG and TG conformers of DPA and the G conformer of PTAB are significantly less stabilized by steric repulsions between the CH_3(N) and (C)CH_3 groups. © 1997 Elsevier Science B.V.

Keywords: Intramolecular C–H···N hydrogen bond; Conformation; Infrared and Raman spectra; *N*,*N*-Dimethylpropylamine; Propyltrimethylammonium bromide

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1. Introduction

Intramolecular and intermolecular interactions play an important role in the structural stabilization of molecules in many chemical and biological systems. One of the most important interactions is hydrogen bonding of the type A–H···B, where A is an atom such as oxygen and nitrogen being more electronegative than hydrogen, and B is an electron donor such as oxygen, nitrogen and halogens [1–3]. Other important interactions, which are attractive and may be regarded as hydrogen bonding, are those of the types C–H···O and C–H···N. In 1962, Sutor proposed the existence of a C–H···O hydrogen bond [4,5]. Taylor and Kennard showed later the

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* Corresponding author. Fax: +81 824 24 7407; e-mail: kohno@sci.hiroshima-u.ac.jp

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crystallographic evidence for an intermolecular C–H···O hydrogen bond and possible existence of a C–H···N hydrogen bond [6]. Desiraju has further studied the C–H···O hydrogen bond in crystals [7,8].

The conformational stability of the OC–CC bond in dialkyl ethers and alcohols has been studied extensively by experimental and theoretical methods [9–14]. These studies have shown that the gauche conformation for this bond is as stable as, or more stable than, the trans conformation. This conformational stabilization is explained by an intramolecular CH···O interaction, which may be called more specifically the intramolecular 1,4-CH···O interaction. Another important interaction is the intramolecular 1,5-CH···O interaction, which stabilizes the gauche–gauche′ conformation of the OC–C–OC bonds in 1,2-dimethoxyethane and its derivatives [15–23].

On the analogy of the intramolecular CH···O interaction, an intramolecular CH···N interaction is anticipated to occur in relevant compounds. To study the possible existence of the intramolecular 1,4-CH···N interaction, we have investigated in this work the conformational stability of *N*,*N*-dimethylpropylamine (DPA), $(CH_3)_2NCH_2CH_2CH_3$, by infrared and Raman spectroscopy and ab initio molecular orbital (MO) calculations. The conformation of a structurally related compound, propyltrimethylammonium bromide (PTAB), $Br(CH_3)_3NCH_2CH_2CH_3$, was also studied for comparison.

2. Experimental

DPA was prepared by mixing dimethylamine with sodium hydrogencarbonate and 1-bromopropane [24]. The product was purified by distillation and the purity was checked by gas chromatography. PTAB was prepared by reacting trimethylamine in ethanol with 1-bromopropane [25]. The product was recrystallized from a mixture of dried ethanol and diethyl ether. PTAB was treated in a dry box purged with nitrogen gas, because this material was highly hygroscopic.

The infrared spectra were measured for DPA in an argon matrix and the liquid state and for PTAB in the solid state. The spectra in the liquid state and the solid state (Nujol mull) were recorded on a Nicolet Impact 400 infrared spectrometer using a DTGS detector by co-addition of 200 scans at a resolution of 1 cm^{-1}. The matrix-isolation infrared spectra were recorded on a JEOL JIR-40X Fourier transform spectrophotometer equipped with a TGS detector by co-addition of 100 scans at a resolution of 1 cm^{-1}. Mixed gas of Ar/DPA = 1000 was slowly deposited onto a CsI plate kept at 11 K by an Iwatani CryoMini D105 refrigerator.

The Raman spectra were measured for DPA in the liquid and glassy states and in 30% aqueous solution, and for PTAB in the solid state and in 30% aqueous solution on a JEOL JRS-400D spectrophotometer with an NEC GLG3200 argon ion laser. The Raman spectra of DPA in the glassy state were measured for the sample contained in an ampoule held on a copper block cooled with liquid nitrogen.

3. Calculations

Ab initio MO calculations were performed on DPA and propyltrimethylammonium (PTA) ion by the restricted Hartree–Fock method using the 6-31G** basis set. The energies, molecular geometries and vibrational wavenumbers were calculated for all of the possible conformers of these compounds. The calculated wavenumbers were scaled by a factor of 0.93 in the region below 1030 cm^{-1} for DPA or below 1040 cm^{-1} for PTA and by a factor of 0.90 in the region above 1030 or 1040 cm^{-1} up to 1500 cm^{-1}, where the vibrations are associated primarily with the methyl and methylene deformations. These values of the scale factor were chosen in the light of the results of the calculations on *n*-pentane and *n*-hexane [26]. The computation in this work was carried out with the GAUSSIAN 94 program [27] at the Information Processing Center of Hiroshima University. The input data for GAUSSIAN 94 were prepared by a molecular modeling and molecular graphics program, MOLDA for Windows [28].

4. Results and discussion

4.1. Energies of conformers

Table 1 gives the relative energies and the skeletal torsion angles for five possible conformers of DPA and two possible conformers of PTA ion, along with

Table 1
Relative energies and skeletal torsion angles for possible conformers of *N*,*N*-dimethylpropylamine (DPA) and propyltrimethylammonium (PTA) ion

Conformer	Relative energy[a] (kcal mol^{-1})	Torsion angles (°)[b]				Number of the gauche conformation for the $CH_3N–CH_2CH_2$ bond[c]	Other important conformations involved
		$\tau(C_aN–CC)$	$\tau(C_bN–CC)$	$\tau(C_cN–CC)$	$\tau(NC–CC)$		
$(CH_3)_2N–CH_2–CH_2CH_3$							
G′G	0.00	69.7	196.1		58.1	1	gauche′-gauche for the LN–$CH_2–CH_2CH_3$ bonds[d,e]
GT	0.07	164.2	– 69.6		187.0	1	
TT	0.88	– 66.5	66.5		180.0	2	
GG	3.06	168.9	– 64.5		101.8	1	gauche′-gauche for the $CH_3N–CH_2–CH_2CH_3$ bonds[f]
TG	3.37	– 80.9	57.2		66.7	2	gauche′-gauche for the $CH_3N–CH_2–CH_2CH_3$ bonds[f]
$(CH_3)_3N^+CH_2–CH_2CH_3$							
T	0.00	– 61.1	61.1	180.0	180.0	2	
G	3.39	– 77.3	45.7	164.6	68.6	2	gauche′-gauche for the $CH_3N–CH_2–CH_2CH_3$ bonds[f]

[a] Calculated at the RHF/6-31G** level. 1 kcal = 4.184 kJ.

[b] C_a, C_b and C_c are the methyl carbon atoms bonded to the nitrogen atom.

[c] A repulsive interaction occurs between the CH_3(N) and (C)CH_2(C) groups.

[d] L denotes the lone pair.

[e] An attractive interaction (the intramolecular 1,4-C–H···N hydrogen bonding) occurs between the hydrogen atom of the (C)CH_3 group and the nitrogen atom.

[f] A repulsive interaction occurs between the CH_3(N) and (C)CH_3 groups.

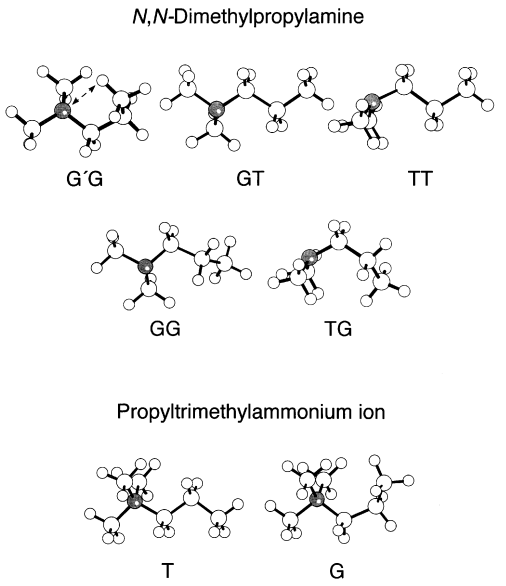

Fig. 1. Structures of five possible conformers of *N*,*N*-dimethylpropylamine (DPA) and two possible conformers of propyltrimethylammonium (PTA) ion. The dashed arrow indicates an intramolecular C–H···N hydrogen bond.

the number of the gauche conformation for the $CH_3N–CH_2CH_2$ bond and other important conformations involved. The structures of these conformers are shown in Fig. 1. For DPA, the three conformers with gauche′–gauche (G′G), gauche–trans (GT) and trans–trans (TT) around the $LN–CH_2–CH_2CH_3$ bonds, where L denotes the lone pair, are more stable than the gauche–gauche (GG) and trans–gauche (TG) conformers by roughly 3 kcal mol^{-1}. For PTA, the trans (T) conformer is more stable than the gauche (G) conformer by 3.4 kcal mol^{-1}. The much higher energies for the GG and TG conformers of DPA and the G conformer of PTA are obviously associated with strong steric repulsions between the CH_3(N) and (C)CH_3 groups, which are close to each other owing to the gauche′–gauche conformation for the $CH_3N–CH_2–CH_2CH_3$ bonds.

It is noteworthy that the G′G form is the most stable conformer of DPA. The origin of this high stability is explained by peculiar conformational dispositions, involved only in this form, of the lone pair on the nitrogen atom and the (C)CH_3 group; namely, they are in the gauche′–gauche conformation. This conformational disposition leads to proximity of the nitrogen atom and one of the hydrogen atoms of the (C)CH_3 group. The ab initio calculations in fact give a nonbonded distance between this hydrogen atom and the nitrogen atom to be 2.76 Å which is close to a sum of the van der Waals radii of these atoms, 2.7 Å. These results indicate that an appreciably strong attractive interaction occurs between the methyl hydrogen atom and the nitrogen atom separated by three carbon atoms. This interaction may therefore be called the intramolecular 1,4-C–H···N hydrogen bonding. It is also noted that the length of the C–H bond involved in this interaction is shorter than the length of the normal C–H bonds; namely, the calculated length for the interacting C–H bond in the G′G conformer is 1.0833 Å, while the lengths for other C–H bonds in the same methyl group are 1.0861 and 1.0868 Å. This is the same structural tendency as found for the 1,4-CH···O interaction [14] and the 1,5-CH···O interaction [29].

The difference in the conformational stability between the GT and TT conformers of DPA, both of which have the trans $NCH_2–CH_2CH_3$ bond, is due to the different number of the gauche conformation for the $CH_3N–CH_2CH_2$ bond involved in the respective conformers. The difference in the conformational stability between the GG and TG conformers is also explained by the different number of the gauche conformation for the $CH_3N–CH_2CH_2$ bond.

4.2. Spectral analysis and conformation of N,N-dimethylpropylamine (DPA)

The Raman spectra of DPA in the liquid and glassy states and in aqueous solution are shown in Fig. 2. The observed wavenumbers and approximate relative intensities are listed in Table 2, where the calculated wavenumbers and intensities for the most stable three conformers, G′G, GT and TT, are also given. The assignments of the observed bands to the particular conformers are almost straightforward owing to the accurate results of the calculations. The crystalline solid state of this compound was not obtained in spite of several attempts by different methods, possibly because of the crystallization competition between the two equally stable conformers, G′G and GT, in the low-temperature liquid.

The spectra in Fig. 2 indicate that some of the bands change their intensities when going from the liquid state to the low-temperature glassy state. The bands

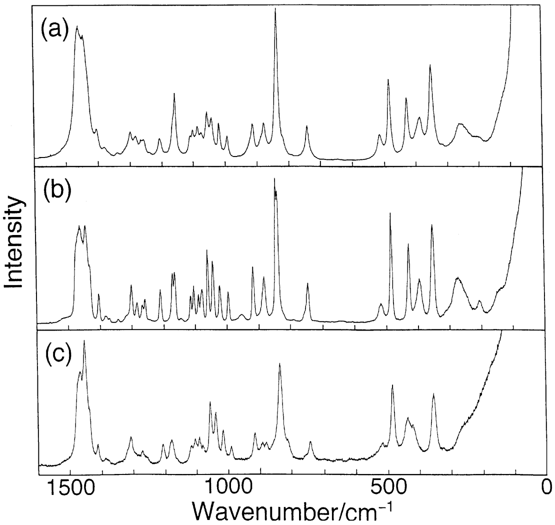

Fig. 2. Raman spectra in the region below 1600 cm^{-1} of *N,N*-dimethylpropylamine (DPA): (a) the liquid state at 295 K, (b) the glassy state at 80 K and (c) aqueous solution at 295 K.

that increase their intensities are those at 487, 842, 916, 1043, 1057, 1167, 1261 and 1303 cm^{-1}. These bands, except for the bands at 1057 and 1303 cm^{-1}, are assigned exclusively to the GT conformer, and the 1057 and 1303 cm^{-1} bands are assigned primarily to this conformer (Table 2). Most of the bands observed for this compound in the liquid and glassy states are assigned consistently to the GT and G′G conformers. The bands that are assigned exclusively to the G′G conformer are observed at 744, 837 and 880 cm^{-1}. The weak bands at 823 and 889 cm^{-1}, whose intensities decrease in going from the liquid state to the glassy state, are assigned to the TT conformer. No bands are observed that are assignable to the GG and TG conformers. From the spectral assignments and the observed intensity behavior discussed above, it is shown for DPA that the three conformers are present in the liquid and glassy states with their relative stabilities in the order GT > G′G > TT.

Comparison of the Raman spectrum of DPA in the liquid state with that in aqueous solution shows that the bands due to the GT conformer at 487, 1043, 1057 and 1303 cm^{-1} and those due to the TT conformer at 823 and 889 cm^{-1} increase in their intensities in aqueous solution, but the bands due to the G′G conformer at 744, 837 and 880 cm^{-1} decrease in aqueous solution. These observations indicate that the GT and TT conformers are more stabilized and the G′G conformer is less stabilized in aqueous solution than in the neat liquid.

The infrared spectra of DPA in an argon matrix are shown in Fig. 3. The observed wavenumbers and relative intensities are given in Table 2. Most of the bands observed immediately after the sample deposition at 11 K are associated with the G′G and GT conformers. Of these, the bands at 745, 831, 878, 1043, 1062 and 1162 cm^{-1}, which are all assigned to the G′G conformer (Table 2), obviously increase in their intensities relative to other bands on the annealing of the matrix. This intensity behavior indicates that the G′G conformer is the most stable in the matrix, since the annealing process induces a transformation of less stable conformers trapped in the matrix at lower temperatures into the most stable conformer. Examination of the observed band intensities shows that the predominant conformers present in the matrix are G′G and GT, but a small amount of the TT conformer is also present in the matrix, as a band at

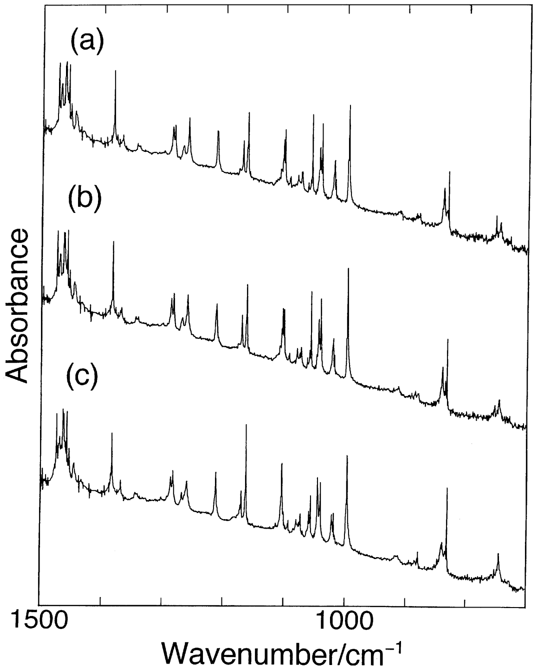

Fig. 3. Infrared spectra in the 700–1500-cm^{-1} region of *N,N*-dimethylpropylamine (DPA) in an argon matrix (Ar/DPA = 1000) with successive annealing: (a) immediately after the deposition at 11 K, (b) after the annealing at 29 K for 5 min and (c) after the annealing at 38 K for 5 min.

Table 2
Observed and calculated vibrational wavenumbers[a] and intensities for *N*, *N*-dimethylpropylamine (DPA)

ν^{b}_{obs} (cm^{-1})						ν^{c}_{calc} (cm^{-1})		
Infrared[d]			Raman			G′G conformer	GT conformer	TT conformer
Matrix (11 K)	Matrix (38 K)	Liquid (295 K)	Liquid (295 K)	Glass (80 K)	Aq. soln. (295 K)			
1474 vs	1474 vs			1473 sh,vs	1471 sh,vs	1482,	1485,	1490,
1470 s	1469 s					1480,1479,	1481,1473,	1477,1477,
1464 vs	1464 vs	1466 vs	1464 vs	1464 s	1465 vs	1470,1468,	1471,1465,	1468,1465,
1462 vs	1462 vs	1461 vs				1461,1459,	1465,1459,	1464,1458,
1457 vs	1457 vs					1455,1450	1458,1452	1453,1442
1453 m	1453 m				1452 vs			
1446 m	1445 w	1446 sh,s	1447 vs	1447 s	1440 sh,m			
1405 vs		1403 vw	1407 m	1406 m	1412 w	1421(5,8)	1423(4,6)	1422(2,7)
1383 vw	1383 vs	1382 s	1384 vw	1384 vw	1385 vw	1401(19,2)	1409(15,1)	1396(5,2)
1374 w		1371 sh,w				1395(5,3)	1394(2,1)	1391(15,0)
1368 w	1368 w			1371 vw				
1345 vw	1345 vw					1354(11,1)		1349(9,6)
1341 vw	1341 vw	1341 w	1342 vw	1345 vw				
		1309 sh,w			1315 sh,vw		1325(6,3)	
		1302 w	1303 m	1305 m	1308 w		1310(11,14)	1305(12,1), 1303(18,0)
1286 m	1286 m	1284 m	1286 m	1286 w		1298(16,5)	1290(21,0)	
1282 m	1282 m					1295(15,4)		
1268 w	1268 w	1266 sh,m	1269 w	1269 w	1270 vs	1270(8,8)		1283(2,11)
1260 s	1259 m	1259 s	1261 w	1260 w	1260 sh,vw		1266(7,4)	
1213 s	1212 s	1208 m	1209 m	1211 m	1206 w	1218(10,3)	1222(11,1)	1217(8,0)
1170 m	1170 m	1167 m	1167 sh,m	1172 m	1179 w		1177(18,3)	
1162 vs	1162 vs	1161 m	1162 s	1165 m	1163 sh,vw	1170(18,3)		1162(14,1)
1110 vw		1112 sh,m	1111 m	1114 m	1115 vw		1110(9,3)	
1103 m	1103 s	1103 s	1103 m	1104 m	1103 w	1101(15,3)		1097(13,4)
1101 s	1100 w							
1092 w	1092 w		1087 m	1089 m	1090 w	1091(2,4)	1098(10,6)	1087(8,6)
1079 w	1079 w					1076(1,1)	1079(1,2)	1084(10,3)
1073 w	1072 w	1074 m	1076 m	1078 m	1081 vw			
1062 w	1058 w					1056(21,7)		
1056 vs	1055 m	1056 s	1057 m	1060 s	1057 m		1048(22,10)	1047(12,6), 1046(38,10)
1043 s	1044 s					1038(18,7)		
1040 vs	1039 s	1042 vs	1043 m	1043 s	1040 m		1036(24,10)	
1020 m	1021 m	1019 s	1021 m	1022 m	1017 w		1027(8,5)	1019(3,8)
1018 w	1018 m							
996 vs	996 vs	994 s	995 m	996 m	991 vw	1013(20,7) 930(1,2)		
991 br,vw	911 vw	914 w	916 m	916 m	916 w		921(2,3)	
883 vw		889 w	889 sh,w	888 sh,vw	893 w		893(1,3)	899(15,7), 889(0,0)
878 vw	878 w	879 vw	880 m	881 m	881 w	877(4,7)		
839 m	839 m	837 s	842 sh,s	844 vs	838 vs		852(19,11)	

Table 2 Continued

ν^{b}_{obs} (cm^{-1})						ν^{c}_{calc} (cm^{-1})		
Infrared[d]			Raman			G′G conformer	GT conformer	TT conformer
Matrix (11 K)	Matrix (38 K)	Liquid (295 K)	Liquid (295 K)	Glass (80 K)	Aq.soln. (295 K)			
831 s	831 vs		837 vs	838 vs		842(8,10)		
			823 sh,w	824 sh,vw	816 sh,w			827(3,10)
753 m	753 vw	753 m		754 sh,vw	753 sh,vw		754(1,0)	
745 m	745 m	743 m	744 m	745 m	744 w	750(6,5)		
728 vw	728 vw							744(2,0)
		514 vw	516 w	521 w	518 vw	515(1,2)		514(9,4)
		487 vw	487 s	487 s	484 s		488(1,3)	
			431 s	432 s	436 m	436(0,0)	428(1,1)	425(0,0)
			391 m	398 m	421[e] w	393(4,0)	379(9,0)	390(7,0)
			353 s	354 s	354 s	345(5,1)	347(0,2)	
			322 vw		325 vw	301(0,0)		306(2,1)
				277 m			259(1,0)	
			262 m	262 sh,w	260 sh,w	247(1,0)	242(0,0)	246(0,0), 245(1,0)
						230(0,0)	232(0,0)	235(0,0)
			206 vw	207 w		198(1,0)	191(0,0)	200(2,0)
			122 br,vw	139 w		126(0,0)		
							110(0,0)	113(0,0)
						55(0,0)	63(0,0)	77(0,0)

[a] Wavenumbers higher than 1500 cm^{-1} are not given in this Table.

[b] Approximate relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

[c] Calculated at the RHF/6-31G** level. For scale factors, see text. The infrared intensities in km mol^{-1} and the Raman intensities in Å^4 amu^{-1} are given in parentheses in this order. The intensities are not given for vibrations higher than 1400 cm^{-1}.

[d] Infrared spectra were not measured below 400 cm^{-1}.

[e] The wavenumber is shifted possibly because of the hydrogen bonding with water.

728 cm^{-1} is assigned to this conformer. No bands, which may be assigned to the GG and TG conformers, are observed in the spectra. The conformational stability of DPA in an argon matrix is accordingly in the order G′G > GT > TT.

The experimental conformational stabilities of DPA evaluated from the spectral analysis for the liquid and glassy states, aqueous solution and an argon matrix are now discussed by comparing with the results from the ab initio MO calculations. Since the results for the matrix represent the conformational stabilities of isolated molecules, they can be compared directly with the theoretical results. The experimental order of the conformational stabilities, G′G > GT > TT, agrees with the prediction by the ab initio calculations. The high stability of the G′G form is explained, as mentioned before, by the formation of an intramolecular hydrogen bond between the hydrogen atom of the (C)CH_3 group and the nitrogen atom. The present spectroscopic finding, as combined with the theoretical interpretation, thus evidences the existence of the intramolecular 1,4-C–H···N hydrogen bond. The predominant existence of the two conformers, G′G and GT, in the matrix is consistent with the calculated small energy difference (0.07 kcal mol^{-1}) between these conformers.

In the liquid and glassy states, the GT conformer is the most stable. The high stability of this form may arise from the formation of intermolecular hydrogen bonds between the hydrogen atoms of the CH_3(N) group and the nitrogen atom of other molecules. In aqueous solution, the GT and TT conformers are more

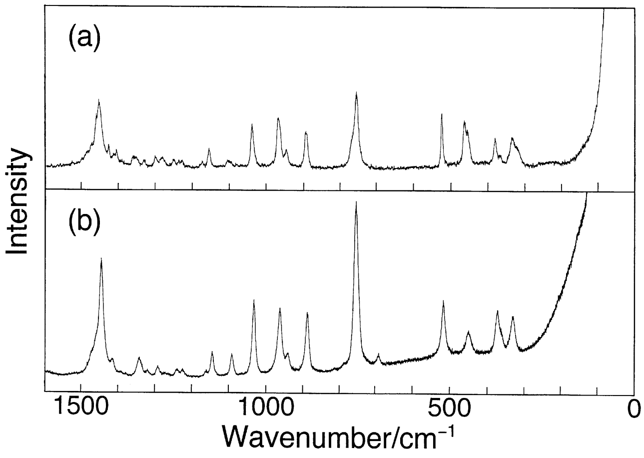

Fig. 4. Raman spectra in the region below 1600 cm^{-1} of propyltrimethylammonium bromide (PTAB): (a) the solid state at 295 K and (b) aqueous solution at 295 K.

stabilized, but the G′G conformer is less stabilized, than in the neat liquid. This conformational behavior in water may be explained by the formation of more significant hydrogen bonds between the nitrogen atom of DPA and water molecules. In aqueous solution, the effect of this O–H···N hydrogen bond should be strong enough to convert the G′G conformation stabilized by the intramolecular C–H···N hydrogen bond into other conformations such as GT and TT. The effect of the hydrogen bonding with water is observed in the spectra as a large wavenumber shift of the band at 391 cm^{-1} in the neat liquid to 421 cm^{-1} in aqueous solution (Fig. 2 and Table 2). This band is, according to the calculated results, associated primarily with the skeletal deformation vibration, in which the nitrogen atom is involved.

4.3. Spectral analysis and conformation of propyltrimethylammonium bromide (PTAB)

The Raman spectra of PTAB in the solid state and in aqueous solution are shown in Fig. 4, and the observed and calculated wavenumbers and intensities are given in Table 3. The infrared spectrum in the solid state has been reported previously [25]; the present spectrum agrees with the previous one. The calculated results indicate that most of the wavenumbers for the T and G conformers are similar. The bands assigned only to the T conformer are those at 754, 764 and 948 cm^{-1} in the Raman spectrum in the solid state. In aqueous solution, an additional weak, but well-defined band is observed at 697 cm^{-1} in the Raman spectrum. This band is assigned to the symmetrical N–C stretching vibration of the $(CH_3)_3NCH_2$ group in the G conformer. The counterpart vibration for the T conformer is prominently observed at 761 cm^{-1} in aqueous solution. These spectral observations, in conjunction with the calculated conformational energies (Table 1), indicate that only the T conformer exists in the solid state, and the T and G conformers coexist in aqueous solution.

To study the conformational stabilities of the T and G conformers in aqueous solution, the enthalpy difference between these conformers was evaluated from the relative Raman intensities of the 761- and 697-cm^{-1} bands at different temperatures. The enthalpy difference, $H_G - H_T$, was evaluated to be 2 kcal mol^{-1}, which implies that the abundance of the G conformer is 10% at 323 K. This result is consistent with the abundance of 12% obtained by NMR for D_2O solution of PTAB at the same temperature [30]. The smaller energy difference for aqueous solution than the calculated result for PTA (3.4 kcal mol^{-1}) may be explained by the effect of possible intermolecular interactions in the solution.

5. Conclusions

The vibrational spectroscopic measurements and the ab initio MO calculations have clarified the

Table 3
Observed and calculated vibrational wavenumbers[a] and intensities for propyltrimethylammonium bromide (PTAB)

ν^{b}_{obs} (cm^{-1})			ν^{c}_{calc} (cm^{-1})	
Infrared[d]	Raman		T conformer[e]	G conformer
Solid	Solid	Aq. soln.		
	1473 m	1474 sh,m	1493, 1485, 1479, 1476, 1472, 1464, 1459, 1456, 1455, 1447, 1446	1492, 1485, 1482, 1480, 1469, 1465, 1461, 1454, 1449, 1446, 1444
	1458 sh,s			
	1451 vs	1451 vs		
1425 s	1425 m	1419 m	1423(2,3), 1421(4,2)	1422(4,3), 1421(4,4)
1411 m	1413 w		1405(2,1)	1409(5,4)
1403 s	1405 w		1396(3,2)	1375(4,2)
	1360 w		1345(10,10)	
1349 m	1351 w	1347 m		
1329 m	1330 vw	1325 vw	1326(3,2)	1336(10,4)
1299 w	1299 w	1296 w	1294(0,8)	1294(6,5)
1283 w	1283 w		1280(12,0)	1276(10,1)
1249 s	1250 vw	1244 w	1244(9,1)	1243(9,3)
1236 vw	1237 vw		1228(4,1)	1219(3,4)
1229 vw	1229 vw	1229 w		
1170 w	1173 vw	1167 vw	1161(0,3)	1150(1,2)
1153 m	1154 m	1150 m	1135(1,6)	1128(2,4)
1104 sh,w	1104 vw		1082(0,1)	1082(1,2)
1098 m	1098 vw	1096 m	1079(2,2)	1069(1,2)
1079 vw			1053(0,0)	1053(0,0)
1038 s	1039 s	1038 s	1031(11,14)	1038(5,4)
967 vs	967 s	967 s	980(32,8), 978(26,8)	981(26,6), 978(26,6)
947 vs	948 w	947 m	946(29,3)	
				925(44,12)
892 vs	893 s	894 s	895(27,9), 893(3,1)	899(12,4)
				846(13,3)
				792(2,5)
768 sh,m	764 sh,s		757(4,0)	
754 s	754 vs	761 vs	749(0,12)	
		697 w		688(0,13)
523 s	523 s	523 s	523(0,4)	530(1,2)
463 sh,w	464 s	455 m	453(1,1)	451(0,0)
453 m	456 sh,s		450(1,0)	438(0,1)
				404(0,0)
	381 m	377 s	370(0,2)	
	370 w	367 sh,m	361(0,0)	365(0,1)
	335 m	336 s	326(0,1)	325(0,0)
	327 sh,m		296(0,0)	310(0,0)

[a] Wavenumbers higher than 1500 cm^{-1} and lower than 290 cm^{-1} are not given in this Table.

[b] Measured at 295 K. Approximate relative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad.

[c] Calculated at the RHF/6-31G** level. For scale factors, see text. The infrared intensities in km mol^{-1} and the Raman intensities in Å^4 amu^{-1} are given in parentheses in this order. The intensities are not given for vibrations higher than 1440 cm^{-1}.

[d] Infrared spectra were not measured below 400 cm^{-1}.

[e] Only this conformer exists in the solid state.

conformational stabilities of DPA and PTAB in various states. In an argon matrix, the conformational stability of DPA is in the order G′G > GT > TT, which agrees with the prediction by ab initio calculations. The experimentally confirmed high stability of the G′G conformer indicates that an appreciably strong attractive interaction occurs between the methyl hydrogen atom and the nitrogen atom. This interaction may be called the intramolecular 1,4-C–H···N hydrogen bonding. In the liquid and glassy states, the GT conformer is the most stable due possibly to the formation of intermolecular C–H···N hydrogen bonds. In aqueous solution of DPA, the GT and TT conformers are more stabilized than in the neat liquid. This conformational behavior of DPA in water may be explained by the formation of more significant intermolecular hydrogen bonds between the nitrogen atom of DPA and water molecules. For PTAB, only the T conformer exists in the solid state, and this conformer is more stable than the G conformer in aqueous solution. The GG and TG conformers of DPA and the G conformer of PTAB are significantly less stabilized by steric repulsions between the CH_3(N) and (C)CH_3 groups.

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